

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$

Temperature Dependence of free energy

$$G = H - TS$$

$$H = E + pV$$

$$G = E + pV - TS \quad \rightarrow (1)$$

for infinitesimal change,

$$dG = dE + PdV + Vdp - Tds - SdT$$

from FLOT

$$dE + pdV = dq \quad \rightarrow (2)$$

$$dG = dq + Vdp - Tds - SdT \quad \rightarrow (3)$$

for a reversible change, $dq = Tds$

$$dG = Tds + Vdp - Tds - SdT$$

$$dG = Vdp - SdT \quad \rightarrow (4)$$

in an isobaric change, $dp = 0$

$$(dG)_p = -SdT \quad \rightarrow (5)$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \rightarrow (6)$$

Substitution of (6) in eqⁿ (5)

$$G = H + T \left(\frac{\partial G}{\partial T}\right)_p$$

$$G - T \left(\frac{\partial G}{\partial T}\right)_p = H \quad \rightarrow (7) \text{ (Gibbs-Helmholtz eqⁿ)}$$

On dividing (7) by T^2

$$\frac{G - T \left(\frac{\partial G}{\partial T}\right)_p}{T^2} = \frac{H}{T^2}$$

$$-\frac{\partial (G/T)}{\partial T}$$

$$\left(\frac{\partial (q/T)}{\partial T} \right)_P = -\frac{K}{T^2}$$

$$\left(\frac{q}{T} \right)_P = - \int \frac{K}{T^2} \cdot dT + I$$

$$d(T^{-1}) = -T^{-2} dT = dT = -T^2 d(1/T)$$

$$\left(\frac{\partial (q/T)}{\partial (1/T)} \right)_P = K$$

for state (1)

$$q_1 = K_1 + T \left(\frac{\partial q_1}{\partial T} \right)_P$$

state (2)

$$q_2 = K_2 + T \left(\frac{\partial q_2}{\partial T} \right)_P$$

$$\Delta q = \Delta K + T \left(\frac{\partial \Delta q}{\partial T} \right)_P$$

$$\boxed{\frac{\partial (\Delta q / T)}{\partial T} = -\frac{\Delta K}{T^2}}$$

$$A = E - TS$$

$$dA = dE - Tds - sdt$$

$$dE = dq + dw = dq - PdV \quad (\text{only } P-V \text{ work})$$

$$dA = dq - PdV - Tds - sdt$$

at constant T and V

$$(dA)_{T,V} = dq - Tds$$

for reversible change, $dq_{rev} = Tds$

$$(dA)_{T,V} = 0$$

$$(\Delta A)_{T,V} = 0$$

for irreversible,

$$dq_{irr} < dq_{rev}$$

$$Tds > dq_{irr}$$

$$dq_{irr} - Tds < 0$$

Spontaneous,

$$(\Delta A)_{T,V} < 0$$

in terms of q

$$dq = dq + vdp - Tds - sdT$$

at constant T and P

$$(dq)_{T,P} = dq - Tds$$

for reversible $dq_{rev} - Tds$

$$(dq)_{T,V} = 0$$

$$(dq)_{T,P}^{irr} < 0 \Rightarrow \text{irreversible spontaneous}$$

$$(\Delta q)_{T,P} < 0$$

in terms of S

$$\Delta S_{total} = 0$$

$$\Delta S_{total} > 0 \text{ spontaneous / irreversible}$$

$$dq = dU - dw$$

$$dq_{rev} = Tds$$

$$dq_{irr} < dq_{rev}$$

$$dq_{irr} < Tds$$

$$\therefore dq < Tds$$

$$Tds > dU - dw$$

$$Tds > dU + PdV$$

$$ds > \frac{dU}{T} + \frac{PdV}{T}$$

$$(ds)_{T,V} > 0$$

Maxwell Thermodynamic Relations

$$dU = Tds - PdV$$

$$dA = Tds + vdp$$

$$dH = -sdT - PdV$$

$$dq = -sdT + vdp$$

alternate -ve and PdV to vdp

Two times same Tds and when sdT (-ve) introduces

System of Variable Composition

PARTIAL MOLAR QUANTITIES

$$G = f(T, P, n_i, n_j)$$

$$\partial G = \left(\frac{\partial G}{\partial T} \right)_{P, n_i, n_j} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_i, n_j} dP + \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} dn_i + \left(\frac{\partial G}{\partial n_j} \right)_{T, P, n_i} dn_j$$

at $dT = 0, dP = 0$

$$\left(\frac{\partial G}{\partial n_i} \right)_{T, P} = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} dn_i + \left(\frac{\partial G}{\partial n_j} \right)_{T, P, n_i} dn_j$$

$$(dG)_{T, P} = G_{ipm} dn_i + \gamma_{jpm} dn_j$$

$$G_{ipm} = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} \rightarrow [\text{Partial molar property}]$$

It is a change in G when one mole of i component is added when there is no appreciable change in concⁿ

The partial molar volume is v_i in an ideal solution will be equal to its molar volume in the pure state. It is not true in the case of non-ideal solutions.

Eg:-

At 50 mass % of ethanol in water at 45°C (half C_2H_5OH and half H_2O)

$$V_{pm}(C_2H_5OH) = 56.76 \text{ cm}^3 / \text{mole}$$

$$V_{pm}(H_2O) = 17.37 \text{ cm}^3 / \text{mole}$$

$$V^*(C_2H_5OH) = 58.65 \text{ ml} / \text{mole}$$

$$V^*(H_2O) = 18.07 \text{ ml} / \text{mole}$$

(* → pure state)